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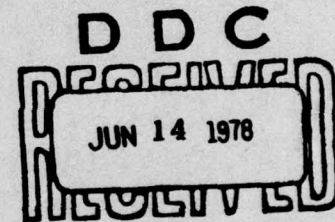
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THERMAL ENERGY ANALYSIS OF DIMETHYLNITROSAMINE AND ITS RECOVERY IN SOIL AND WATER

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This technical report has been reviewed and is approved for publication.

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THERMAL ENERGY ANALYSIS OF DIMETHYLNITROSAMINE AND ITS RECOVERY IN SOIL AND WATER

INTRODUCTION

The increased concern for potential cancer-causing agents, including N-nitrosamines, has caused scientists to develop several methods for the analysis of these compounds. Published methods by Fine et al. (1, 2, 3) have resulted in the development of the Thermal Energy Analyzer, coupled with the Gas Chromatograph (GC-TEA), which is reported to be specific for nitrosamines. The limit of detectability for this instrument has been reported in the parts per trillion range.

The analysis of N-nitrosamines involves extraction and concentration in an appropriate solvent for injection into the GC-TEA. This paper describes the development of a method for recovery of dimethylnitrosamine (DMN) from soil and water which gives good accuracy, repeatability, and minimum detectable levels of 0.10 $\mu\text{g/g}$ and 0.10 $\mu\text{g/ml}$ for soil and water respectively.

MATERIALS AND METHODS

Dry samples of soil (1 g) and distilled water (5 ml) were spiked with aqueous solutions of DMN in several absolute amounts (1.0, 0.50, 0.20, and 0.10 μg). The spike in soil was thoroughly mixed and shaken, then extracted with 10 ml of distilled water and centrifuged at 4000 RPM for 10 minutes. Five-ml aliquots of the supernatant were extracted three times with 5-ml portions of dichloromethane (DCM). The combined extracts were collected in a concentrator tube with 1 ml of isooctane as

1. Fine, D. H., et al. Group analysis of volatile and nonvolatile N-nitroso compounds. *Nature* (London) 247:309 (1974).

2. Fine, D. H., et al. Description of the thermal energy analyzer for trace determination of volatile and nonvolatile N-nitroso compounds. *Anal Chem* 47:1188 (1975).

3. Fine, D. H., and D. P. Roundbehrer. Trace analysis of volatile N-nitroso compounds by combined gas chromatography and thermal energy analysis. *J Chromatogr* 109:271 (1975).

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a keeper, placed in a 60° water bath, and allowed to evaporate to a final volume of 1.0 ml \pm 0.10 ml. Twenty μ l of this final concentrate were injected into the GC-TEA for analysis. Five ml of the distilled water samples, after spiking with DMN, were thoroughly mixed and extracted three times with DCM and treated in the same manner as the soil combined extracts. Twelve replications for each concentration were analyzed.

The solvent dichloromethane (DCM) was used in the extraction process for two reasons: (1) it facilitated sample cleanup due to DMN being readily soluble in DCM, and (2) the low boiling point of DCM simplified concentration. Isooctane was the solvent in which DMN was finally concentrated.

The GC-TEA parameters were as follows:

Gas Chromatograph Varian Model 2800

Carrier gas: 100% Argon Flow rate: 22 ml/min
Column: 6 ft X 1/8 in OD, SS 10% FFAP, Chromosorb W AW,
80-100
Oven Temperature: 200°C
Injector temperature: 160°C
Line temperature: 165°C
Sample size: 20 μ l

Thermal Energy Analyzer Model 502

Furnace temperature: 425°C
Cold trap temperature: -150°C
Vacuum: 3.5 mmHg
Water pressure: 10-15 PSI
Attenuation: 4

Analytical reagent grade dichloromethane and isooctane were used. Deionized-distilled water was used for all water samples. All glassware, including pipets, syringes, collection and extraction apparatus, was acid washed and thoroughly rinsed with deionized-distilled water.

A stock solution containing 100 ppm of DMN in isooctane was prepared from pure DMN. Serial dilutions of this stock solution provided DMN standards in 1, 5, 10, and 25 ppm concentrations. A standard curve was prepared by 1- μ l injections of these standards at the reported GC-TEA conditions. Peak heights were measured and a standard curve was obtained (Figure 1). The recovered DMN in isooctane from the soil and water samples was injected into the GC-TEA and the peak heights were measured. Calculation of the percent recovery was made by using the following formulas:

$$\frac{(H_u)(V_1)(A_1)}{(H_s)(V_2)(A_2)} \times C_s \times V_c = \mu\text{g/ml Recovered}$$

$$\frac{\mu\text{g/ml Recovered}}{\mu\text{g/ml Added}} \times 100 = \% \text{ Recovered}$$

where:

- H_u = Peak height of unknown, mm
- V_1 = Volume of unknown injected, μl
- A_1 = Attenuation at which unknown was injected
- H_s = Peak height of standard, mm
- V_2 = Volume of standard injected, μl
- A_2 = Attenuation at which standard was injected
- C_s = Concentration of standard, $\mu\text{g/ml}$
- V_c = Volume of concentrate, ml

RESULTS

The measured recoveries for DMN are shown in Table 1. DMN was shown to be readily recoverable from soil and water at concentrations as low as 0.10 $\mu\text{g/g}$ and 0.10 $\mu\text{g/ml}$ respectively. Generally the percent recovery was found to be independent of concentration in both soil and water samples. The recovery mean was higher for water samples than for soil samples in three of the four concentrations; however, statistically, the mean was larger for only the 1.0 and the 0.1 concentrations ($P < .01$ and $P < .05$, respectively). The variability of the recovery appeared to depend upon the percentage recovered.

DISCUSSION--CONCLUSIONS

Although 0.10 $\mu\text{g/g}$ in soil and 0.10 $\mu\text{g/ml}$ in water were the lowest recovery concentrations attempted, we do not intend to establish this level as the lowest detectable limit. More sophisticated equipment and exotic extraction methods may result in acceptable recoveries at lower concentrations. This method is a quick and reliable method of obtaining consistent recoveries of dimethylnitrosamine from soil and water at these concentration levels.

Most analytical methods for volatile nitrosamines include distillation and solvent extraction followed by concentration of the extract.

This technique requires considerable time and attention of the investigator in addition to the use of elaborate distillation and extraction apparatus. To overcome such problems, we found that by aqueous extraction followed by centrifugation, DMN could be extracted from soil with minimal losses. This technique could be applied to any of the volatile nitrosamines.

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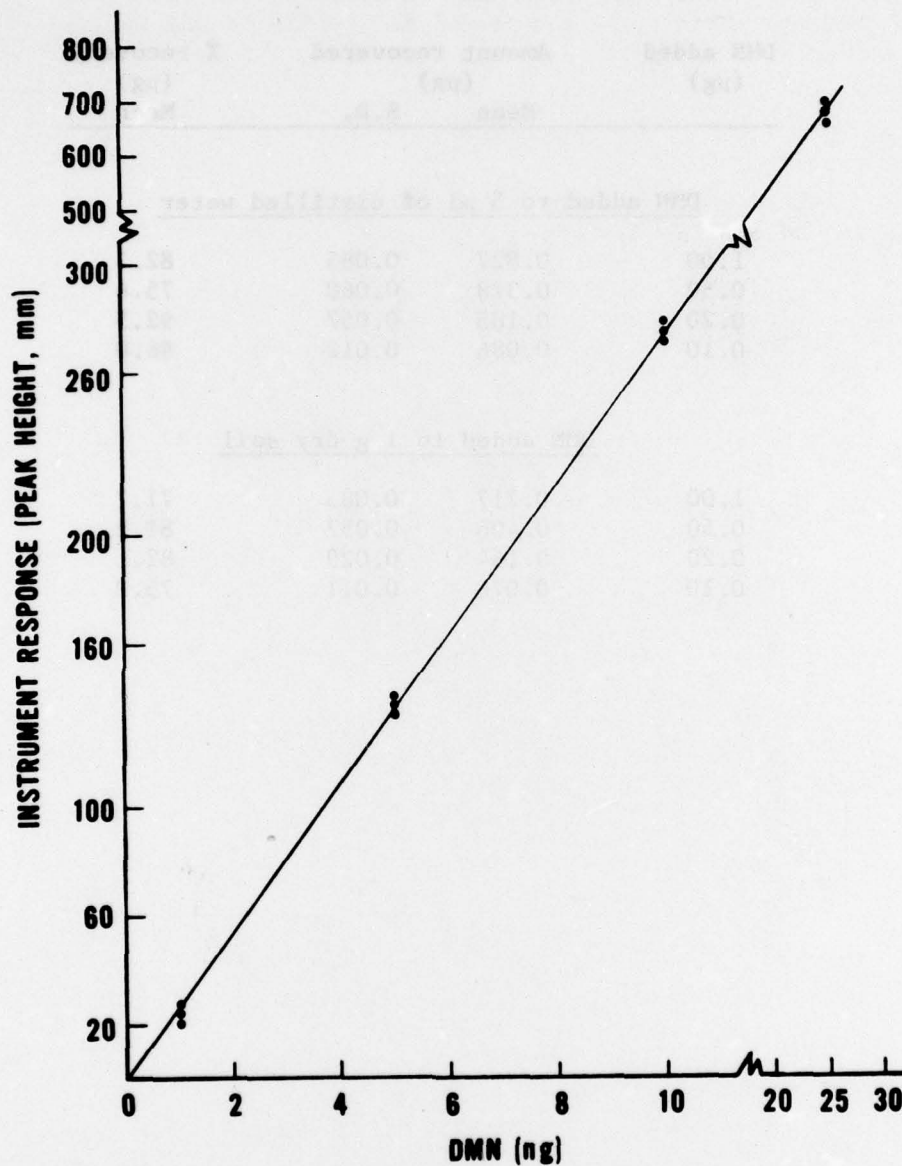


Figure 1. Gas chromatograph-thermal energy analyzer (GC-TEA) calibration for DMN.

TABLE 1. DIMETHYLNITROSAMINE (DMN) RECOVERIES
ADDED TO WATER AND SOIL

DMN added (μg)	Amount recovered (μg)		% recovery (μg)
	Mean	S.D.	Mean

DMN added to 5 ml of distilled water

1.00	0.827	0.085	82.7
0.50	0.378	0.060	75.6
0.20	0.185	0.057	92.5
0.10	0.086	0.012	86.0

DMN added to 1 g dry soil

1.00	0.717	0.083	71.7
0.50	0.406	0.057	81.2
0.20	0.164	0.029	82.1
0.10	0.076	0.011	75.8